NUCLEATION CHAMBER FOR CRYSTAL GROWTH

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13 Claims

BACKGROUND OF THE INVENTION

This invention provides a sublimation furnace for the growing of crystalline material from the vapor state. In particular it provides a cylindrical nucleation chamber having opposed conical heat sinks at either end to assist in growing larger crystals of device quality material over a greater area of the inner periphery of the chamber than prior art chambers. The walls of the chamber can be of carbon or silicon carbide coated guaze material but preferably is of porous graphite. The nutrient material surrounds the outside of the chamber and vapor permeates the chamber walls. The nucleation chamber may be rotated during crystal growth to minimize heat spots from occurring in the walls of the chamber.

Some monocristalline platelets of materials are grown by decomposing a charge of the material in bulk form and then condensing the vapor. A source of heat to decompose the bulk material and the bulk form are so arranged as to cause supersaturation of the bulk material within a cavity within the charge of material itself. At high supersaturation levels, random nucleation will often occur on the walls of the cavity. As the supersaturation within the cavity decreases, monocristals of the material will often grow as platelets, with the faces of the platelets oriented towards those areas which dissipate the energy of supersaturation by radiation. U.S. Pat. 3,275,415 Hung Chi Chang and Leonard J. Kroko, and assigned to the assignee of the present invention, describes the construction and the operation of a sublimation furnace for growing monocristalline platelets from the vapor state.

Crystal nucleation occurs randomly upon the inside wall of the cavity. Often times, many crystals nucleate and grow in a small area of the cavity wall surface. When the radiation path from a growing crystal is blocked by adjacent growing crystals, the rate of growth is changed and, at times, even arrested. The result is that the crystal will often contain voids and is usually intergrown with adjacent crystals. This crystal which is a result of the growing process is undesirable since most device applications require that the crystal be uniformly grown and free of crystalline intergrowths.

SUMMARY OF THE INVENTION

In accordance with the present invention and in attainment of the foregoing objects there is provided a furnace for growing single crystals of sublimating materials comprising an empty hollow nucleation chamber disposed within the furnace, the chamber having porous walls and closed ends, each of said ends comprising a centrally disposed conical surface and a flat outer peripheral surface integral with the base of the conical surface, the conical surface projecting into the nucleation chamber, a crucible constructed to contain at least one material selected from the group consisting of silicon carbide, a mixture of silicon and carbon, boron nitride, aluminum nitride and subliming refractory carbides, nitrides, and silicides, the material surrounding the chamber, and heat ing means disposed about the crucible to heat it and the contained material to a temperature sufficient to cause evolution of vapors of the material within the crucible and passage thereof through the porous walls of the nucleation chamber whereby the vapors of the material can concentrate at nucleation areas of the nucleation chamber and grow into the hollow thereof.

An object of this invention is to provide apparatus for producing monocristalline bodies of material which are uniformly grown and free of crystalline intergrowth.

Another object of this invention is to provide apparatus for producing monocristalline bodies of material which are uniformly grown and free of crystalline intergrowth wherein the apparatus is designed to minimize random crystal nucleation and to increase the disipation of the energy of condensation by radiation.

Other objects of this invention will, in part, be obvious and will, in part, appear hereinafter.

DESCRIPTION OF THE INVENTION

For a better understanding of the nature and objects of the present invention, reference should be had to the following drawings, in which:

FIG. 1 is a view, partly in cross-section, showing a nucleation chamber disposed in a crucible;

FIG. 2 is a view, partly in cross-section and partly in elevation of a sublimation furnace, suitable for the production of single crystals in accordance with the teachings of this invention;

FIG. 3 is a view, partly in cross section of an alternate construction of the nucleation chamber of FIG. 1; and

FIG. 4 is a view, partly in cross-section and partly in elevation, of an alternate construction of the sublimation furnace of FIG. 2.

The apparatus taught in this invention is suitable for the growth of single crystals of any material that sublimes and evidences no liquid phase at ordinary conditions. It also includes materials which if they exhibit a liquid phase at all, the conditions at which the liquid phase occurs would be impractical for single crystal growth. Such materials generally tend to decompose, at least in part in the vapor state. Representative materials of this nature and to which the present invention applies includes boron nitride, aluminum nitride, silicon carbide, and subliming refractory carbides, nitrides and silicides.

In order to describe the invention more fully and for no other purpose, the apparatus will be described for the growing of single crystals of silicon carbide. With reference to FIG. 1, there is shown a thin walled nucleation chamber 10. The chamber 10 comprises a hollow cylindrical member 12 and ends 14 and 16. Each of the ends 14 and 16 comprises respectively a brim portion 18 and 20, and a centrally disposed hollow conical portion 22 and 24. The apex of each cone 22 and 24 may touch each other.

Cylindrical member 12 is made of commercially available, high purity graphite, as by machining such a shape from a block of graphite. A graphite cylinder facilitates control of the temperature gradient in the crystal growth area. Moreover, it provides a smooth, near isothermal surface for nucleation by virtue of its comparatively high coefficient of thermal conduction. As a practical matter,
3,525,594

3. Shapes other than cylindrical can be used for these purposes. However, a shape that defines a symmetrical cavity, and preferably a circular cylindrical shape, is desirable to facilitate both fabrication thereof and maintenance of temperature control during use. The ends 14 and 16, side of graphite, are provided at the ends of the chamber to prevent the raw materials from entering into the nucleation area.

The wall of the cylindrical member 12 is relatively dense but sufficiently powdery or powdery porous to permit the passage of predetermined amounts of the silicon carbide vapor. The wall thickness suitably is relatively thin, generally being on the order of about 2 to 12 mils. The actual size of the member 12 being used depends on such factors as the size of the furnace, the character of the heating means and similar considerations.

A coarse grained graphite cylinder having a high gas permeability of 0.018 darcys, for example, that sells as CCO grade graphite whose average grain size is about 0.006 mm., having walls from 0.008 to 0.010 inch thick gives excellent results. Silicon carbide vapors penetrate the walls to the desired extent and when after operation of the chamber, spaced a predetermined distance of extremities, the large silicon carbide crystals covers the central portion of the inner walls. A much denser grade of graphite, CMB grade, consists of extremely fine grains of an average of 0.003 mm. and is relatively impermeable to passage of silicon carbide vapors if the wall thickness exceeds 0.005 inch. Problems arise in making and handling a graphite vessel with walls this thin, and consequently the less dense, coarser grained graphite cylinders are preferred. Graphite bodies of densities of 1.73 to 1.50, of an average grain size of 0.004 to 0.016 mm., and a gas permeability of 0.005 darcys or more will result in good cylinders.

However, fine holes can be drilled through a cylinder made from any grade of graphite to permit passage of silicon carbide vapors to the interior. In such cases, the wall thickness is not particularly critical.

Surrounding the nucleation chamber 10 is a charge 26 of raw materials disposed in a graphite vessel 28. The charge can be silicon carbide particles, such as commercial silicon carbide crystals, or a mixture of elemental silicon and carbon, or both. For the best results the raw material charge should be packed as densely as possible. Finely divided silicon carbide, for example, 20 mesh to 100 mesh, 0.06 inches in diameter, having a high density. One of the advantages of the apparatus of this invention is that its operation is not restricted to the use of silicon carbide as a source of vapor, although that can be used. Thus elemental silicon and carbon may be used in place of silicon carbide. Silicon and carbon are commercially available in high-purity form; consequently, with the use of pure carbon and silicon fewer undesirable impurities enter the system than when the usual commercial silicon carbide crystals are used. Silicon and carbon will react to provide silicon carbide prior to reaching operating temperatures and consequently vapors of silicon carbide will be evolved from the mass 26. The mass 26 of raw materials including the chamber 10 is disposed in the carbon crucible 28 to provide support for the outside surface of the raw material mass.

Referring now to FIG. 2, the vessel 28 containing the nucleation chamber 10 and the mass 26 is disposed in the furnace 30 on a suitable support and the furnace 30 can be any shape desired. The furnace 30 has an outside water cooled jacket 32. The jacket 32 may be made of any suitable metal such, for example, as steel or copper. A cover wall 34 is joined to the top of the jacket 32 in substantially a gas tight relationship through use of gaskets 36 and such having a central aperture 48 and 50. A hollow support assembly 51 is affixed to the aperture 48 of the plate 42.

Disposed within the jacket 32 and supported by the base assembly 38 is a shield member 52, preferably made of molybdenum. Disposed within the member 52 is an outside graphite shield 54 and an inside graphite shield 56 spaced apart from each other. Disposed in the space between shields 54 and 56 is insulating material 58 preferably powdered carbon.

Within the confines of the inside graphite shield 56 is situated a split hollow cylindrical graphite heater 60 which is split vertically in two places, 180° apart, for a distance of approximately 1/3 of its length. The heater 60 is bolted to water cooled electrodes 62. Within the heater 60 is disposed a deep drawn graphite cup member 64 which has an outwardly extending flange 66 which supports the member 64 within the heater 60. Disposed on the inside bottom surface of the member 64 is a hollow graphite cylinder 68 having a plurality of apertures in its side wall. Disposed on top of the cylinder 68 is a graphite cup-shaped member 70 partly filled with insulating material, preferably powdered carbon. Centrally disposed within, and supported by, the member 72 is a covered hollow cylinder 74 with cooling fins 76 attached to the bottom thereof. The cylinder 74 is partly filled with insulating material, again preferably powdered carbon. The function of the cooling fins 76 is to reduce radiation heat loss from the vessel 28.

Passing upwardly between the water cooled electrodes 62 is a tube 78 which passes through a cup-shaped member 80, partly filled with insulating material, preferably powdered carbon, through the bottom of the member 64 and into the cylindrical member 68.

It has been found advantageous for control purposes and ease of charging, discharging and maintenance to provide entry ports along one side and the top. These can take the form of manhole entry ports having covers 82 and 84, which are attached to vessel 30 in a substantially gas-tight relationship by means of bolts 86 and suitable gaskets 88 and the like. A sight tube 89 extending from one side of vessel 28 may be provided for making observations and measurements and the like.

It will be noted that the heater 60 surrounds the side wall of the nucleation chamber 10 and extends beyond its ends a substantial distance. This disposition of the heater 60 along with the character of the nucleation zone material contributes to the development of crystal growth lines, or heat flow lines, having relatively long straight portions at the center of the hollow cylinder 12. It is apparent therefore that the wall of the cylinder 12 is hot and the ends 14 and 16 are cooler, relatively speaking. Consequently, heat from the heater 60 flows towards the wall, into the cylinder 12, and then to the surfaces of the conical portions 22 and 24, and thence to the brim portions 18 and 20 which are at the lowest temperatures.

Vapors of silicon carbide will preferentially condense on nuclef ors or surfaces of the growing crystals of silicon carbide and thereby produce flat single crystal platelets having a central portion and having a surface and the charge 26 is substantially dissipated. The distribution of the silicon carbide platelets on the inside walls of the cylinder member 12 is normally such that the center half of the member 12, for example, the central portion extending 1.5 to 2 inches in a 3 inch long cylinder, will contain most of the crystals and is joined to the most perfect crystals, growing perpendicularly to the wall, while a small region at each end of this central portion will have smaller silicon carbide platelets which are directed at an angle towards the ends 14 and 16 of the
nucleation chamber 10, and the last half inch or more at each end of the member 12 has no platelets growing thereon.

The conical portions 22 and 24 of the respective ends 14 and 16 have a decided influence on the rate of growth and physical characteristics of the single crystals produced. The ends 14 and 16 are really heat sinks and the particular design shown enables the growing crystals to "see" the heat sinks more readily and for a greater period of time during the growth period. The surface of the conical portions 22 and 24 greatly increase the surface area of the heat sink member when compared to prior art heat sink members and enables one to dissipate more thermal energy per unit of time than the prior art members.

As shown in FIG. 1, crystals 90, 92, 94, 96 and 98 nucleated on the inside wall of cylindrical member 12 and are growing by dissipating the energy of condensation by radiation to the heat sink members comprising the conical portions 22 and 24, and the brim portions 18 and 20 of the respective ends 14 and 16. As long as each crystal is able to "see" enough surface area of the heat sink members to readily dissipate its energy of condensation, single crystal growth will continue. It is readily apparent from FIG. 1 that all the crystals will be able to "see" adequate surface areas with a minimum of interference with each other. Crystal 94 is able to readily see both conical portions 22 and 24 and consequently dissipate its energy of condensation equally to both. On the other hand, crystal 96 dissolves most of its thermal energy to conical portion 24. Crystals 98 and 92 are located near the coolest portions of the nucleation chamber 10 and dissipate all their thermal energy to respective ends 14 and 16.

Isotherms 100, shown in FIG. 1, indicate the preferred direction of growth of single crystals since crystal growth proceeds on the temperature gradient lines, that is, in a direction perpendicular to the isothermal lines. Hereinafter "temperature gradient" is a line perpendicular to the isothermal lines. To grow single crystal planar platelets, it is necessary to maintain a maximum temperature gradient along the desired growth line. The disposition of the heating means and the character of the nucleation cylinder, or other symmetrical shape, in this invention provide a set of long growth lines perpendicular to the isotherms 100 shown in FIG. 1. Therefore, with reference to FIG. 3 there is shown a nucleus 110 which is an alternate construction of the nucleation chamber 10. The nucleation chamber 110 comprises a hollow cylindrical member 112 and two end members 114. Each end member 114 comprises a cover plate 116 from which an integral axially disposed member 118 is appended. Mounted endperpendicular to and integral with, the member 118 is one or more fin members 120, each parallel to the cover plate 116.

A conical axially disposed integral member 122 protrudes from the opposing surface of the cover plate 116 from the member 118. Surface 124 of the conical member 122 is designed to conform to the isotherms formed when the chamber 110 is heated. The design shown is to allow for the most efficient and maximum absorption of radiant heat dissipated by the growing single crystals as well as a most efficient means of dissipating the heat absorbed by the conical member 122.

The fins 120 are surrounded by the charge of material from which the crystals are grown. The distance between the fins 120 and only surrounds the cylindrical member 112. Therefore the fins 120 of the ends 114 act as cooling fins to dissipate the absorbed heat faster than the ends 14 and 16 of the chamber 10, FIG. 1.

The chamber 110 comprises the same materials as the nucleation chamber 10. The conical members 122 may be used to produce crystals of nearly any thickness but a thickness of about 0.25 inch is preferred.

When substantially pure argon, or other inert atmosphere, is used during crystal growth, the conductivity type, if any, of the resulting crystals if no controlled doping is applied, is determined by the impurities present in the raw materials. By selecting the purest raw materials, almost intrinsic silicon carbide crystal platelets have been successfully produced. The intrinsic silicon carbide is practically clear or relatively colorless. However, predetermined type conductivity crystals, or crystals with p and n regions in selected order, can be obtained in this invention by, for example, adding to the argon a small amount of impurity from either Group III or Group V of the Periodic Table, as in the form of a chloride. Of course, conditions are maintained to prevent condensation of the doping agent in the argon conduit. Alternatively and preferably, a solid rod of the impurity as such rather than in compound form can be inserted in the argon tube to within the heater area, whereupon it will vaporize and be entrained by the argon. Also it is possible to insert a crucible containing the conductivity impurity in molten form into the tube 78, whereupon the impurity vaporizes and is carried into the nucleation chamber. When doping is to be stopped, the rod or crucible simply is withdrawn.

The timing of the introduction of a significant conductivity impurity can be used to produce a change in the conductivity type of the crystal.

The conditions to be maintained for crystal nucleation and for crystal growth are not the same. To nucleate a crystal requires a state of supersaturation of the vapor of the crystal at the nucleation site. As a practical matter, a high ratio of the supersaturation pressure to the equilibrium pressure at a given temperature is required to cause nucleation in most instances. Such a degree of supersaturation can be attained by a temperature differential within chamber 10 as compared to the charge 26 on the order of 75° to 150° C. lower in the chamber 10 at about 2500° C. After growth has nucleated on the walls of chamber 10 and growth is desired, the temperature difference should be lowered to no more nearly approach identity. Supersaturation to a slight extent, e.g., on the order of that resulting from a temperature differential of 0.1 degree to 10° or even 25° C., at about 2500° C. can be tolerated during growth, because such a small amount thereof will not cause additional crystals to be nucleated.

These partial pressure changes in the silicon carbide vapor are readily brought about through manipulation of the heating means. For example, supersaturation is necessary at the initiation of the production of the crystals. Accordingly, the heater temperature is turned up to high (full power) to generate a large vapor pressure before the temperature at the central portion of the graphite chamber 10, at the growth zone, becomes nearly as high. Hence, the vapor entering the chamber 10 will become supersaturated due to the lower temperature therein. After crystals are nucleated, the temperature differential is lowered so that a vapor pressure of silicon carbide in the chamber 10 is only slightly greater than the equilibrium pressure for the temperature in the chamber. This result flows naturally as a consequence of the rise in temperature of the graphite substrate and the lowering of the temperature on the raw material mass as the heater input is slightly reduced thereby making the equilibrium pressure and the supersaturation pressure of the silicon carbide vapor in chamber 10 approach each other.

As previously indicated an important factor is the provision of adequate flow of silicon carbide vapor through walls of the member 12. While particularly good results have been obtained by making crucible 10 from a graphite having an average particle or grain size of 0.006 mm., a density of 1.62 and a gas permeability of 0.018 darcy, the wall thickness being 0.008 inch, other graphites of considerably greater porosity can be utilized. For example, good crystal growth was obtained on a highly porous graphite cylinder with walls of about 0.25 inch thick, the graphite being grade 60 porous graphite of National Carbon Company, having a density of 1.05,
46.9% relative porosity with an average pore diameter of 0.0013 inch and an average air permeability at 70°F. The air was at 760 mm. pressure, 15% relative humidity.

Using dense graphite, for example, 1.76 and higher density, with an extremely fine grain size of 0.003 mm. or less, and a gas permeability below 0.002 darcys, crucibles of wall thickness of 10 mill or greater will grow no silicon carbide crystals. However, upon drilling a series of fine holes through the walls of such impervious graphite, excellent crystal growth is obtained. The number of silicon carbide nuclei is found to be directly proportional to the area of the holes up to 20% of the wall area of the cylinder. For each one percent of the surface being converted into holes, under conditions of operation of the apparatus, as outlined above, there are 0.625 nucleations per square centimeter of the inner surface of the chamber, as an average.

For a more complete discussion and teaching of the effect which the porosity of the wall members 12 and 112 have upon the nucleation and growth of platelets of single crystals within the nucleation chambers 10 and 110, reference should be had to U.S. Pat. 3,275,415 authored by Hung Chi Chang and Leonard J. Krok, and assigned to the assignees of the present invention, which also describes the operation of a sublimation furnace similar to that shown in FIG. 2.

During operation of the furnace 30 it was discovered that hot spots were occurring within the nucleation chamber 10. This resulted in a non-uniform distribution of grown crystals about the inner periphery of the member 12. The crucible 30 was modified to permit rotation of the vessel 28 and the chamber 10 disposed therein.

With reference to FIG. 4, a graphite shaft 126 is attached to the vessel 28. The shaft 76 passes upwardly through a hollow shaft of the cooling fins 76, through the cover of the cylinder 74, by means of a mechanical joint 128, the shaft 126 is connected to a metal rod 130 passing through cover 82 and a substantially gas tight bearing 132. The rod 130 through a geared connection 134 is connected to a motor 136. During the growth of the crystals, the motor 136 causes rotation of the vessel 28 and the chamber 10 contained therein thereby minimizing the occurrence of hot spots in the member 12. As a result, the crystals grown are more uniform in size and more evenly distributed on the inner periphery of the member 12 and in accordance with the principles of growth from the vapor state.

Additionally, I have found that graphite or silicon carbide coated fabric gauze of the type employed in sanding operations is suitable for constructing the cylindrical members 12 and 112. It has been found that a lot of nucleations occur on the inner periphery of the walls of these gauze members 12 and 112. Good large crystals of material can be grown but not as well with members 12 and 112 made of graphite. In growing silicon carbide crystals, silicon carbide coated fabric gauze having a pore size of 0.5 to 1.0 mm. is found to be satisfactory.

The following is illustrative of the teachings of this invention:

**EXAMPLE I**

A graphite vessel 3 inches in diameter and 6 inches high was packed along its bottom portion with a dense layer of finely powdered pure silicon carbide. A graphite cylinder, approximately 2 inches long and 1.50 inches in diameter and having a wall thickness of 0.010 inch, was placed on a graphite end plate laid on the silicon carbide layer. Another end plate was placed on the cylinder. The graphite cylinder and the end plates were prepared from a relatively porous, coarse grained graphite block and formed the nucleation chamber 10 shown in FIG. 1. The conical positions were 3/16 inch by 3/4 inch in height and had a wall thickness of 3/16 inch. Then the crucible was filled completely with additional quantities of the silicon carbide powder. The prepared crucible was lowered into a furnace made in accordance with the teachings of this invention and as shown in FIG. 2 and the furnace was closed. The furnace was then evacuated to about 10^-5 mm. of mercury to remove gaseous impurities.

The temperature change during the operation of the furnace consisted of four periods; namely, degassing, nucleation, growth, and annealing. The furnace was heated under high vacuum to a temperature of 1800°C. The temperature was then raised to 1800°C ± 10°C and maintained for about an hour to accomplish thorough degassing. Any volatile impurities contained in the furnace which are evolved at these temperatures are removed with the aid of the vacuum being drawn. Commercially available pure argon was then introduced through the tube 78 (FIG. 2) to give approximately one atmosphere pressure.

The temperature of the vessel was raised to 2500°C ±15°C in approximately 20 minutes. The silicon carbide around the graphite cylinder volatilizes rapidly. Nucleation started on the inner walls of the graphite nucleation cylinder as the vapor became supersaturated inside the cylinder. The temperature of the vessel was maintained constant for a period of 6 hours. After holding the furnace at temperature for 6 hours the furnace was slowly cooled for 5 hours to room temperature. After cooling the vessel was removed from the furnace. The nucleation chamber was removed from the crucible and broken open. The platelets of silicon carbide were removed from the graphite cylinder and examined.

The platelets were single crystal and of device quality measuring an average of 5 mm. in diameter.

**EXAMPLE II**

The same procedure was practiced in Example II as was practiced in Example I except the nucleation chamber had flat discs of graphite (see U.S. Pat. 3,275,415 previously referenced) to close the ends of the graphite cylinder. Examination of the single crystal platelets which were grown showed them to be only an average of 3 mm. in diameter. The amount of device quality platelets was 25% less than those produced in the improved nucleation cylinder.

**EXAMPLE III**

The procedure practiced in Examples I and II was repeated except that the duration of the dwell time at the growing temperature of 2500°C ±20°C was 20 hours for each.

Examination of the platelets of silicon carbide crystals grown showed that both nucleation cylinders again produced single crystal device quality silicon carbide. However, the nucleation chamber embodying the teachings of this invention again produced the larger platelets. The platelets of the newly designed nucleation chamber averaged 8 mm. in diameter. The platelets grown in the prior art nucleation chamber averaged 5 mm. in diameter. The number of device quality platelets obtained by growth in the improved nucleation cylinder was 35% more than those obtained from the prior art nucleation chamber.

**EXAMPLE IV**

The procedure practiced in Example I was repeated except for the following:

(a) A homogeneous mixture of commercially available high purity powdered elemental silicon and carbon was packed into the graphite crucible;

(b) The furnace was also initially heated under vacuum to a temperature of 1300°C ±10°C where it was maintained constant until a high vacuum was obtained. The temperature was then slowly raised to 1800°C ±10°C over a period of 35 minutes. Commercially available pure
argon was then introduced through the tube 34 (FIG. 1) to suppress the volatilization of carbon. The process continued for one hour before raising the temperature of the furnace to 2500° C, and

(c) The temperature was maintained at 2500° C, for 20 hours.

Examination of the platelets of silicon carbide revealed that they were single crystal and suitable for semiconductor device fabrication the average size of the platelets was 7 mm. in diameter.

One notes therefore that the improved nucleation chamber produces larger platelets of device quality silicon carbide crystals than those obtainable from prior art nucleation chambers in the same growing period of time. This is accomplished while also producing a greater number of device quality silicon carbide platelets.

It is to be understood, of course, that the inside surface of the nucleation cylinders embodying the teachings of this invention may have selected areas act as predetermined nucleation sites by providing a coating of silicon on these selected areas. However, it is harder to recover platelets from silicon surfaces than from graphite surface because the bond with a silicon surface is stronger.

While the invention has been described and illustrated with respect to the preparation of silicon carbide single crystals, it should be understood that it can be used in preparing single crystals of other materials. For example, in preparing single crystals of aluminum nitride, the apparatus is used as heretofore described but aluminum nitride, rather than silicon and carbon, is present in the raw material. The nucleation surface can perform in the same manner as described heretofore. It should also be understood that in preparing such other crystals, the nucleation chamber or nucleation surface thereof may be made of materials other than graphite such, for example, as silicon carbide or quartz can be used depending on their inertness at the operating temperatures, with respect to the particular compound involved.

While the invention has been described with reference to particular embodiments and example, it will be understood, of course, that modifications, substitutions and the like may be made therein without departing from its scope.

1. A furnace for growing single crystals of sublimating materials comprising:
   (1) A vessel constructed to contain at least one material selected from the group consisting of subliming refractory carbides, subliming refractory nitrates, and subliming refractory silicides;
   (2) A hollow nucleation chamber disposed within said vessel and adapted to be surrounded by said material, said chamber having porous cylindrical walls suitable for providing the formation of nucleation sites at which single crystals will grow and closed ends, each of said ends comprising a centrally disposed inwardly projecting conical body and a flat outer peripheral surface extending to the cylindrical walls; and
   (3) Heating means disposed about said vessel to heat it and the contained material to a temperature sufficient to cause evolution of vapors of the subliming material within the vessel and the passage of the vapors through the porous walls of the nucleation chamber whereby the vapors of the material can concentrate at the nucleation sites of the nucleation chamber and grow into the hollow thereof.

2. The furnace of claim 1 wherein the nucleation chamber is made of graphite.

3. The furnace of claim 1 wherein the nucleation chamber is made of graphite and selected areas of the surface walls of the nucleation chamber have mounted therein a material selected from the group consisting of silicon, silicon carbide and quartz, said material forming preferred nucleation sites for crystals of the material growing within the nucleation chamber.

4. The furnace of claim 1 wherein the nucleation chamber is made of graphite and the vessel is constructed to contain a material selected from the group consisting of silicon carbide, and a mixture of silicon and carbon, and preselected areas along the inside surface of the walls of said nucleation chamber being coated with silicon to form preferred nucleation sites for the growth of crystals of silicon carbide.

5. The furnace of claim 1 wherein the porosity of the walls of the nucleation cylinder is caused by holes passing through an otherwise non-porous wall in amount equal to from 0.1 to 20% of the wall area, the surface of the interior walls of the hollow member consisting of a material other than said vaporized material and characterized by being less favorable nucleation sites than the solid grown material itself whereby a relatively small number of nuclei of the vaporized material are formed on the interior walls of the hollow member and grow into large single crystals is favored.

6. The apparatus of claim 5 wherein the nucleation chamber is made of graphite and the material within the crucible produces vapors of silicon carbide.

7. The furnace of claim 1 wherein the conical body of each end of the nucleation chamber has a concave surface of a predetermined curvature corresponding to the profile of the isotherms present within the nucleation chamber when the furnace is in operation.

8. The furnace of claim 7 wherein an axially disposed member extends perpendicular from the surface of each end of the nucleation chamber and extends away from the surface of each end opposite from the direction of the projecting conical body, said axially disposed member having at least one flat surface member radially extending perpendicularly outwardly from said member and spaced apart from said ends and from each other flat surface member.

9. The furnace of claim 1 in which the walls of the nucleation chamber are fabricated from a fabric gauze coated with a material selected from the group consisting of carbon and silicon carbide.

10. The furnace of claim 6 in which the walls of the nucleation chamber are fabricated from silicon carbide coated fabric gauze.

11. The furnace of claim 1 and including a means for rotating the nucleation chamber.

12. The furnace of claim 1 wherein the material contained within the vessel is boron nitride.

13. The furnace of claim 3 wherein the material contained within the vessel is aluminum nitride.

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